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**MEASUREMENT OF REFRACTIVE INDICES OF
CDSIP₂ AT TEMPERATURES FROM 90 TO 450 K
(POSTPRINT)**

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Measurement of refractive indices of CdSiP₂ at temperatures from 90 to 450 K

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Abstract: Ordinary and extraordinary refractive indices of CdSiP₂ were measured and a Sellmeier equation was obtained for the first time to our knowledge over the temperature range 90 to 450 K. The index values were used to calculate the crystal temperature and phase-matching angle dependence of the generated wavelengths in the nonlinear frequency conversion of a range of pump wavelengths. A good match was obtained between the calculated values of the wavelengths and some experimental measurements.

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References and links

1. P. G. Schunemann, "CdSiP₂ and OPGaAs: New Nonlinear Crystals for the Mid-Infrared," OSA Tech. Digest (Optical Society of America, 2011), paper A1FA1.
2. F. K. Hopkins, B. Claflin, P. G. Schunemann, N. C. Giles, and L. E. Halliburton, "Potential of CdSiP₂ for Enabling Mid-Infrared Sources," Proc. SPIE **9616**, 96160W (2015).
3. K. Zawilski, P. Schunemann, D. Zelmon, *et al.*, "Growth and characterization of large CdSiP₂ single crystals," J. Cryst. Growth **312**(8), 1127–1132 (2010).
4. P. Brand, B. Boulanger, P. Segonds, V. Kemlin, P. G. Schunemann, K. T. Zawilski, B. Ménaert, and J. Debray "Phase-matching properties and refined Sellmeier equations of the new nonlinear infrared crystal CdSiP₂," OSA Tech. Digest (Optical Society of America, 2011), paper A1FA2.
5. K. Kato, N. Umemura, and V. Petrov, "Sellmeier and thermo-optic dispersion formulas for CdSiP₂," J. Appl. Phys. **109**(11), 116104 (2011).
6. T. S. Moss, S. D. Smith, and T. D. F. Hawkins, "Absorption and dispersion of indium antimonide," Proc. Phys. Soc. B **70**(8), 776–784 (1957).
7. T. Skauli, P. S. Kuo, K. L. Vodopyanov, T. J. Pinguet, O. Levi, L. A. Eyres, J. S. Harris, M. M. Fejer, B. Gerard, L. Becouarn, and E. Lallier, "Improved dispersion relations for GaAs and applications to nonlinear optics," J. Appl. Phys. **94**(10), 6447–6455 (2003).
8. M. Born and E. Wolf, "Principles of Optics," 7th ed. (Cambridge University Press, 1999).
9. S. C. Kumar, M. Jelinek, M. Baudisch, K. T. Zawilski, P. G. Schunemann, V. Kubeček, J. Biegert, and M. Ebrahim-Zadeh, "Tunable, high-energy, mid-infrared, picosecond optical parametric generator based on CdSiP₂," Opt. Express **20**(14), 15703–15709 (2012).
10. P. G. Schunemann, L. A. Pomeranz, K. T. Zawilski, J. Wei, L. P. Gonzalez, S. Guha, and T. M. Pollak "Efficient mid infrared optical parametric oscillator based on CdSiP₂," in Advances in Optical Materials (AIOM) 2009, OSA Technical Digest (Optical Society of America, 2009), paper AWA3.

1. Introduction

The II-IV-V₂ semiconductor CdSiP₂ with uniaxial crystal structure is attractive for nonlinear optical frequency mixing applications because of its high nonlinearity ($d_{36} > 80$ pm/V), adequately large birefringence (-0.05), along with wide bandgap energy (> 2 eV) [1,2]. Since the thermal conductivity of CdSiP₂ (13.6 W/m/K) is relatively modest compared to, say that of GaP (110 W/m/K), it is important to lower the absorption losses in the material to obtain high power frequency conversion. One way to obtain lower absorption is to lower the temperature of the material. Figure 1 shows the infrared transmission in CdSiP₂ measured at 90 K, 295 K, and 450 K with the higher transmission at low temperature indicating possibly

lower losses. However, accurate low temperature-dependent refractive index values for CdSiP₂ are not readily available – although they have been measured at room temperature [3,4]. A thermo-optic dispersion formula for CdSiP₂ has been derived [5] over a temperature range of 10 to 70 °C (283 to 343 K) and a wavelength range of 0.5 to 6.6 μm. In this work we present refractive indices of CdSiP₂ measured over a temperature range of 90 to 450 K in the wavelength range of 0.97 to 9.5 μm.

2. Measurement technique

The method used for refractive index measurement was outlined by Moss [6] and used more recently for accurate measurement of refractive indices of GaAs [7]. A single crystal of CdSiP₂ grown by the Bridgman technique was polished on both sides and thinned to 160 ± 2 μm. The crystal was XZ oriented – that is, the *a*- and *c*-axes, respectively, were in the plane of the surface, and the Y-axis was an *a*-axis perpendicular to the surface. Transmission spectra of the samples were taken using a PerkinElmer FTIR spectrometer run with a step size of 0.125 cm^{-1} over the wavenumber range of 16,667 to 400 cm^{-1} (i.e., wavelength range of 0.6 to 25 μm) and over a temperature range of 78 K to 400 K. Light incident on the sample was polarized using two wire grid polarizers (Thorlabs WP25M-UB and WP25H-K), covering the spectral ranges from 0.25 to 4 μm and 3 to 30 μm, respectively. With light polarized along the crystal X (or *a*) axis, the ordinary index n_o was obtained, and when light was polarized along the crystal Z (or *c*) axis, the extraordinary index n_e was obtained.

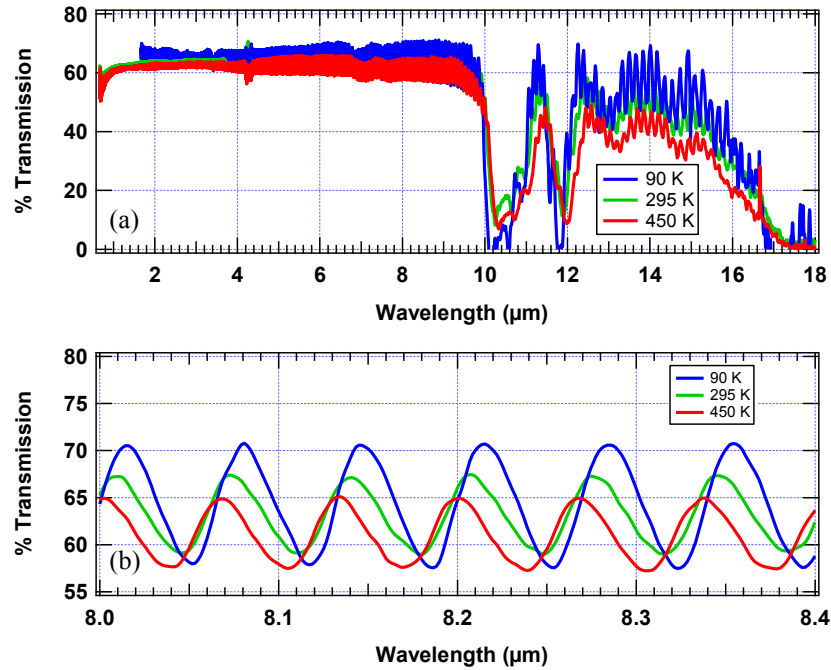


Fig. 1. Temperature dependent FTIR transmission spectra of CdSiP₂ for light polarized along the ordinary axis.

The spectra shown in Fig. 1 exhibited a series of fringes having extrema occurring at specific wavelengths at which the light transmitted through the samples interfered constructively or destructively. If the sample thickness is denoted by d , then constructive interference at a wavelength λ indicates a relationship:

$$2 n(\lambda) d = m \lambda \quad (1)$$

where m is an integer at the fringe maxima.

From the sample thickness (d) and the fringe number (m) the refractive index n can be determined. Since neither parameter can be directly measured with sufficient accuracy, the refractive index values determined from prism measurements [3] were used to determine both the values d and the room temperature fringe number at wavelengths near 1 μm . From the thickness and fringe number, the index values at longer wavelengths and at other temperatures were determined.

3. Results and discussion

From the FTIR spectra of the 160 μm thick wafer, the results of the refractive index measurements over a temperature range of 90 K to 450 K and wavelength range of 0.97 to 9.5 μm from are shown in Fig. 2 and referred to as the ‘experimental values’. They are fitted with a Sellmeier equation of the form

$$n^2 = A(T) + \frac{B(T)}{\lambda^2 - C} + \frac{D}{\lambda^2 - E} \quad (2)$$

and the fit parameters are summarized in Table 1. This form of the Sellmeier equation was chosen to be consistent with the (equivalent) form presented in Ref. [5], and is discussed in Ref. [8] (p. 99, Eq. (38)).

The difference between the ‘experimental values’ shown in Fig. 2 and the values obtained from Eq. (2) is the fit error, which is plotted in Fig. 3. There are possibly various origins of this error, including a) the presence of additional, but weak, resonances not accounted for, b) the particular manner in which temperature-dependence was included (as a polynomial in the coefficients, and not in the resonant frequencies), and c) minor errors in finding fringe peaks from the spectra. Nevertheless, we find good agreement between the experimentally determined phase matching angles and the temperature dependence of idler wavelengths, as will be shown in Section 4.

To our knowledge these are the first cryogenic and above room temperature index measurements for CdSiP_2 .

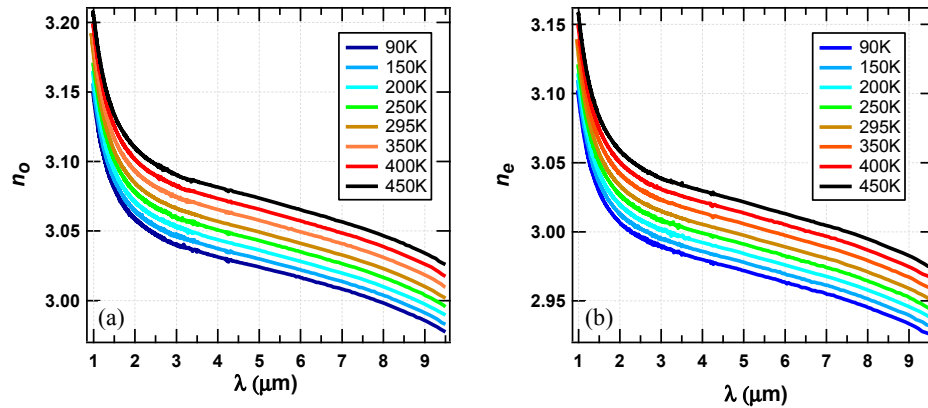


Fig. 2. The experimentally obtained values for the ordinary and extraordinary refractive indices of CdSiP_2 at different temperatures.

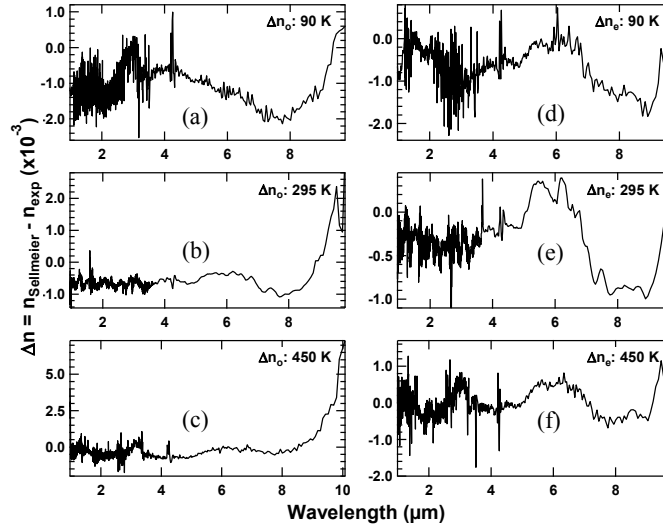


Fig. 3. Fit errors between Sellmeier expressions and experimental refractive index at different temperatures, for both the ordinary (left column) and extraordinary (right column) axes.

Table 1. Temperature-dependent Sellmeier fit coefficients^a

Coef.	n_o	n_e
A	$11.95 + 5.3479 \times 10^{-4} T + 5.5894 \times 10^{-7} T^2$	$11.438 + 5.5408 \times 10^{-4} T + 5.0458 \times 10^{-7} T^2$
B	$0.6134 + 9.4768 \times 10^{-5} T + 2.0148 \times 10^{-7} T^2$	$0.61584 + 3.8668 \times 10^{-5} T + 2.9901 \times 10^{-7} T^2$
C	0.101733	0.11182
D	2334.22	2021.26
E	833.205	777.162

^aThe temperature T is in Kelvin and wavelength λ is in microns. The fits are valid for a wavelength range of 0.97 to 9.5 μm , for temperatures between 90 and 450 K.

4. Comparison of predicted and experimental parametric conversion wavelengths

Temperature dependence of the signal and idler wavelengths obtained by parametric frequency down conversion of pump lasers at wavelengths of 1.064 and 1.99 μm has been presented in the literature [9, 10]. In Ref. [9], the results of optical parametric generation (OPG) of a (pump) laser at 1.064 μm are presented for a 5 mm thick CdSiP₂ crystal cut at a phase matching angle $\theta = 90^\circ$ between the crystal c axis and the propagation direction of light through the crystal. The temperature of the crystal was varied from ~295 K to 425 K and the wavelength of the generated signal beam was measured.

Using the temperature dependent Sellmeier Equations given in Eq. (2), the signal and idler wavelengths satisfying the phase matching condition (for $\theta = 90^\circ$, with the pump beam traveling as an extraordinary wave and the two generated beams traveling as ordinary waves), were determined over a temperature range of 90 to 450 K. These results are shown in Fig. 4, along with the experimental results from Ref. [9]. The calculated wavelengths agree very well with those experimentally measured.

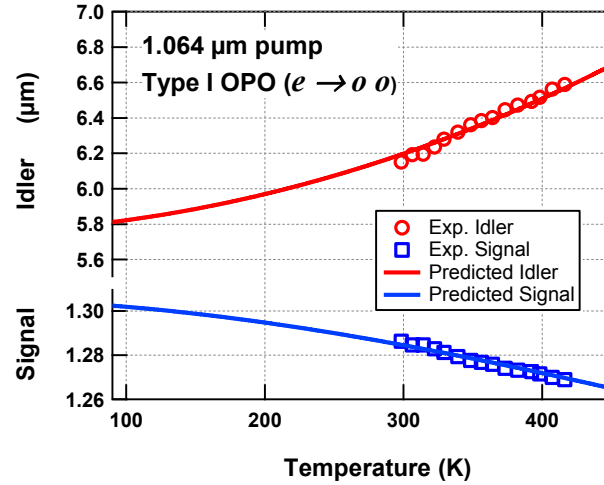


Fig. 4. Comparison between the experimental temperature-dependent idler and signal wavelengths [8] (symbols) and the predictions using temperature-dependent Sellmeier equation (solid lines) for Type I phase matching at critical phase matching angle, and CdSiP₂ is pumped at 1.064 μm.

In the first optical parametric oscillator (OPO) demonstrated in CdSiP₂ with a pump laser at 1.99 μm [10], the generated wavelengths were measured as a function of the crystal orientation (i.e., phase matching angle) at room temperature, or about 295 K (Fig. 5(a)). They were also found as a function of crystal temperature for a fixed phase matching angle (Fig. 5(b)). It is worth noting that by interpolating the experimental data, at 295 K (the temperature for Fig. 5(a)), the idler generated in Fig. 5(b) is 4.38 μm; from the experimental data in Fig. 5(a), this wavelength is generated at a phase matching angle of 46.84° (a little different from the crystal cut of $\theta = 46^\circ$). Using the Sellmeier expressions reported here (Eq. (2)), the best fit to the temperature-dependent data is found at a phase matching angle of 47.04°. If the 0.2° difference between the fit angle and the angle found from the data is attributable to a small error in the reported phase matching angles, then the Sellmeier expressions above well match not only the temperature-dependent data but also the angle-dependent data. (See Fig. 5(a), where the calculated curve was shifted to lower angles by 0.2° to correspond to the experimental values as reported.) The relatively small discrepancy between the theory and experimental results can be attributed to experimental errors in the measurement of the phase matching angle (as discussed), the crystal temperature (either in Ref. [10] or in the measurements reported here), or in our assumption of 295 K for room temperature (as recorded in Ref. [10]).

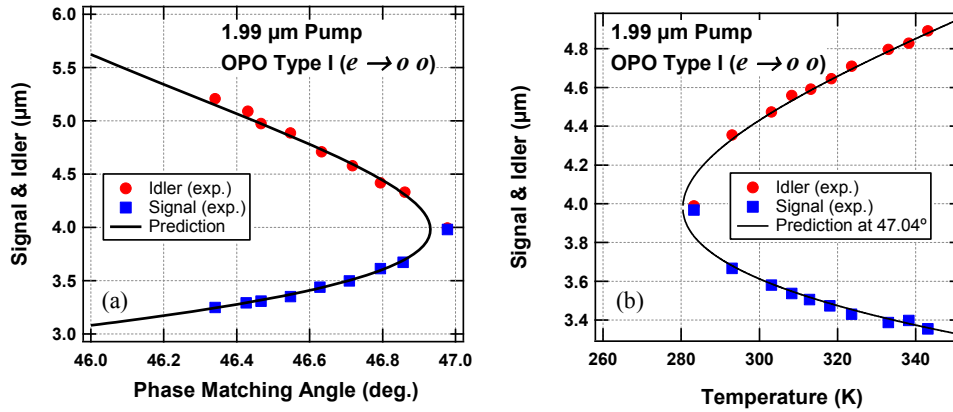


Fig. 5. (a). Comparison of angular dependent between the experimental results (Ref [9], symbols) and the prediction using the Sellmeier equation at 295 K (solid line), shifted by -0.2° (see text); Fig. 5(b), Comparison of temperature dependent signal and idler wavelengths between experimental results (symbols) from Ref [9]. and the prediction using the Sellmeier equation (solid lines).

5. Temperature dependent phase matching curves at different pump wavelengths

The predicted temperature- and angle- dependent phase matching curves provide guidance as to the ideal crystal cut, target operating temperature, polarization type, pump laser wavelength selection, etc. All of these must be a part of the design of a $\chi^{(2)}$ frequency conversion experiment. In what follows, we present the calculations for two special cases of interest, as a function of the pump wavelength. The more general phase matching curves are then given in Figs. 9–14 for a series of temperatures and laser pump wavelengths in the region in which the Sellmeier fits are valid. (In these latter cases, the plots show phase matching out to 10 μm, which is only a small extrapolation from the fit limit of 9.5 μm.)

Non-critical phase matching (i.e., $\theta = 90^\circ$) is desirable in most cases of frequency mixing because the generated wavelengths are not in this case sensitively dependent on the crystal angle. Non-critically phased matched signal and idler wavelengths are shown in Fig. 6 for three temperatures spanning the measured range, employing each of the three phase matching types ($e \rightarrow oo$, $e \rightarrow eo$, $e \rightarrow oe$) which result in phase matching curves falling within the Sellmeier equation's region of validity. Note that for the Type II phase matching curves (dashed and dotted lines), the nonlinear coefficient is zero for a non-critically phase matched crystal. In order to use those curves, one must tune away from $\theta = 90^\circ$; this will recover some finite nonlinear coefficient, but the resulting process will be far less efficient than Type I phase matching.

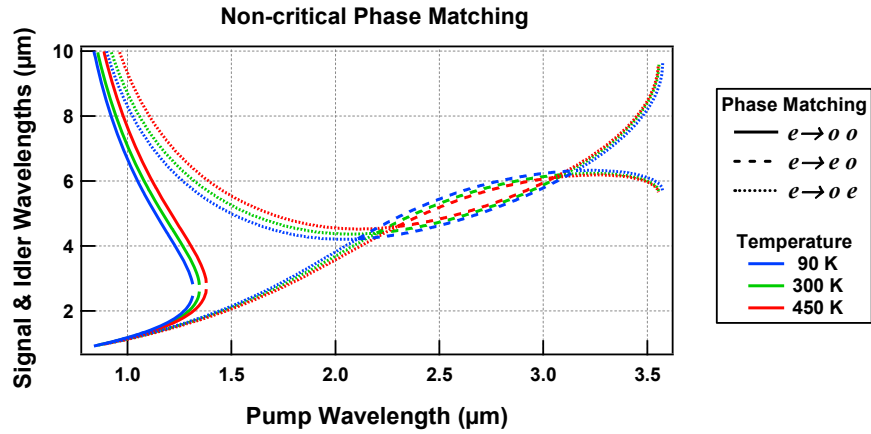


Fig. 6. Non-critical phase matching signal and idler wavelengths as a function of wavelength, temperature, and phase matching type.

The case of degenerate optical parametric generation (the reverse of second harmonic generation) is also frequently of special interest. Figure 7 below shows the angle at which a CdSiP_2 crystal should be cut in order to produce degenerate OPG when pumped at a wavelength between 1.4 and 4.8 μm , at a temperature between 90 K and 450 K.

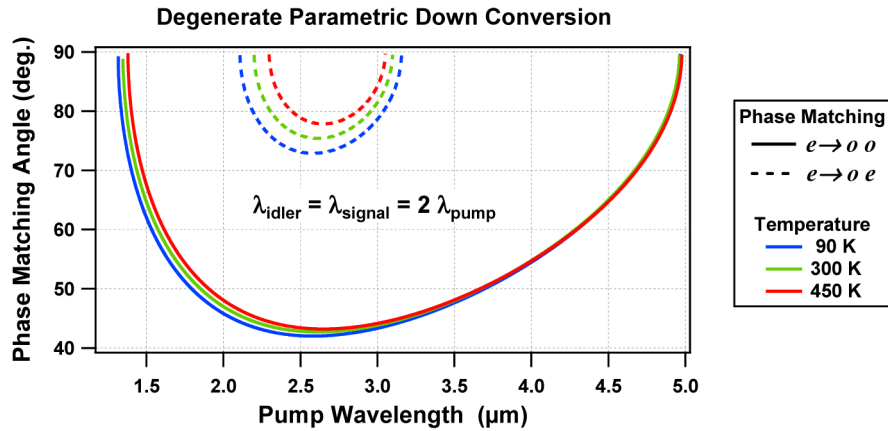


Fig. 7. Phase matching angle for degenerate optical parametric generation at 90 K, 300 K, and 450 K, as a function of the pump laser wavelength. These are shown for the two phase matching types (eeo and oeo) for which phase matching occurs.

Phase matching predictions in CdSiP_2 show a particularly interesting situation when pumped with an extraordinary wave near 2.3 μm . At this pump wavelength, the phase matching curves are almost perfectly vertical: at a fixed angle and temperature, there is simultaneous phase matching over a bandwidth of about 3 μm , depending on the pump wavelength. For a 1 cm thick crystal pumped at 2.34 μm , the value of the $\text{sinc}^2\left(\frac{\Delta kL}{2}\right)$ curve

is above 0.99 over an idler range of 2.2 μm , and the FWHM is 3.1 μm . There is therefore a potential to generate a relatively large bandwidth in this fashion, although it is sensitive to small (0.05°) changes in angle (see Fig. 8(b)). It is worth noting that this feature of simultaneous phase matching across a large bandwidth is present regardless of the operating temperature; at a different temperature, one needs only go to a slightly different crystal angle.

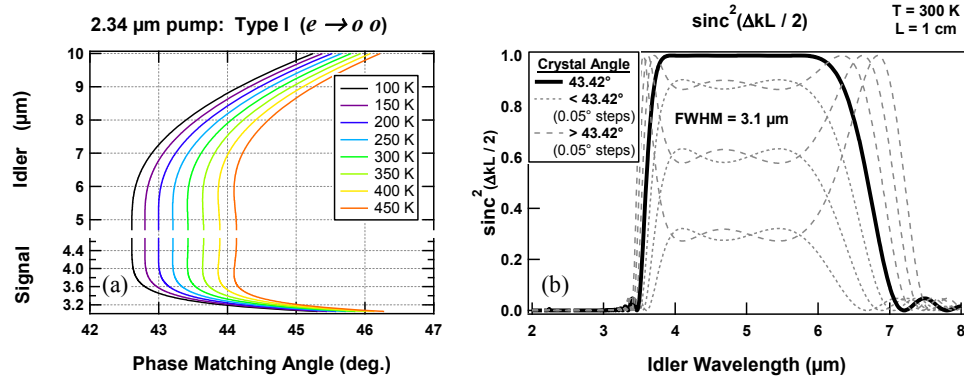


Fig. 8. (a). Phase matching curves for CdSiP₂ pumped at 2.34 μm, for a variety of temperatures. The curves are notable for simultaneously phase matching a broad range of wavelengths; Fig. 8(b). Plot of the sinc^2 function for a 1 cm thick CdSiP₂ crystal held at 300 K, for several crystal angles. This curve is a useful metric for the nonlinear conversion efficiency.

Crystals for optical parametric generation are most commonly pumped at commercially available laser lines. Accordingly, signal and idler wavelengths are plotted for several of these pump wavelengths in Figs. 9–14 below using each of the phase matching types that enable critical phase matching in the short-wave and mid-wave infrared spectral regions. These are shown as a continuous function of crystal angle, for temperatures between 100 K and 450 K.

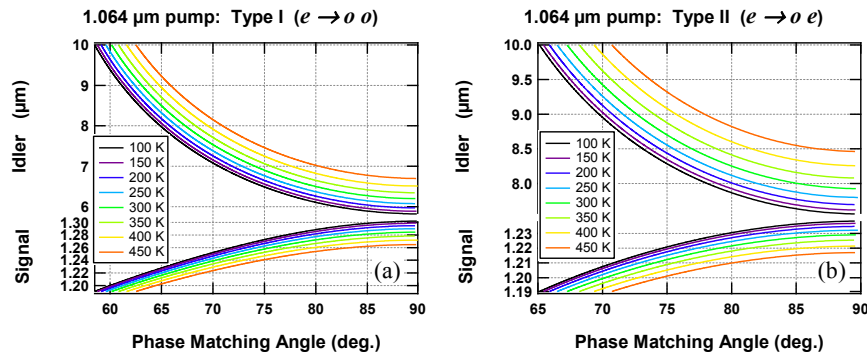


Fig. 9. Phase matching curves for CdSiP₂ pumped at 1.064 μm, for a variety of temperatures. The phase matching types differ between the two figures.

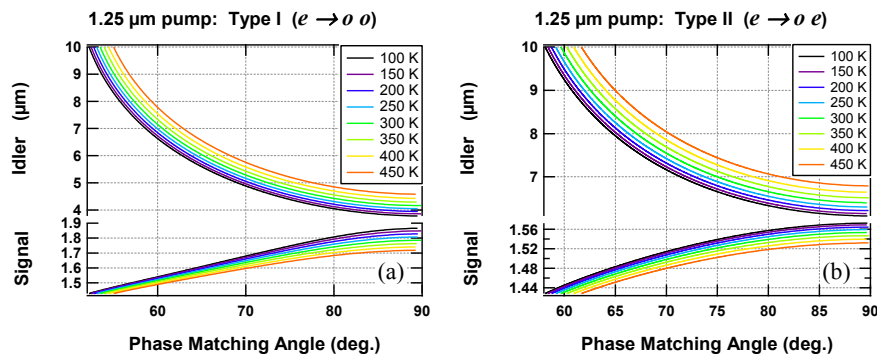


Fig. 10. Phase matching curves for CdSiP₂ pumped at 1.25 μm, for a variety of temperatures. The phase matching types differ between the two figures.

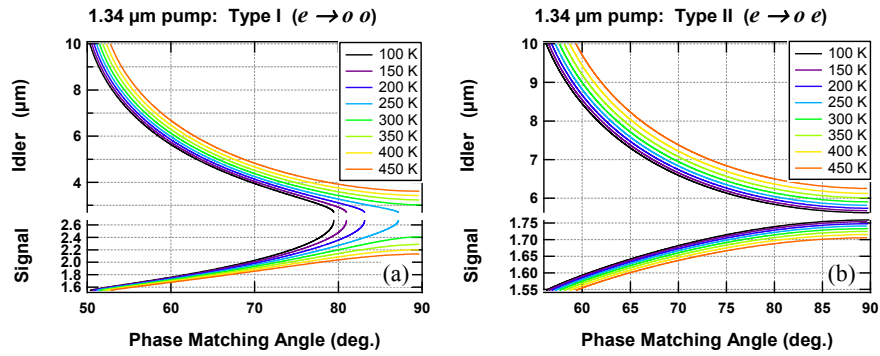


Fig. 11. Phase matching curves for CdSiP₂ pumped at 1.34 μm, for a variety of temperatures. The phase matching types differ between the two figures.

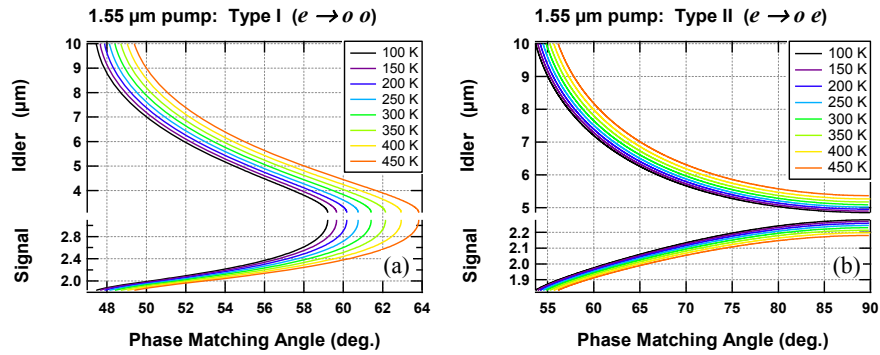


Fig. 12. Phase matching curves for CdSiP₂ pumped at 1.55 μm, for a variety of temperatures. The phase matching types differ between the two figures.

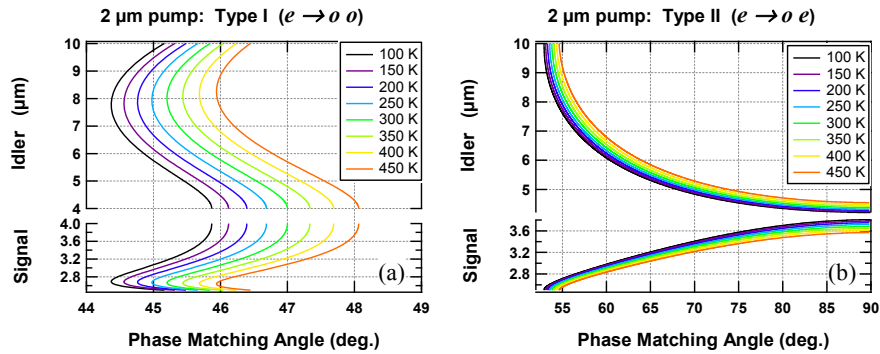


Fig. 13. Phase matching curves for CdSiP₂ pumped at 2.00 μm, for a variety of temperatures. The phase matching types differ between the two figures.

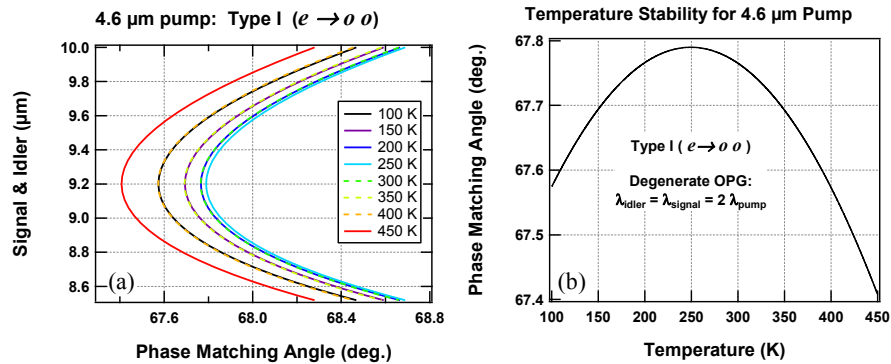


Fig. 14. (a). Phase matching curves for CdSiP₂ pumped at 4.6 μm, for a variety of temperatures. The phase matching angle attains a maximum between cryogenic and elevated temperatures, as seen in Fig. 14(b), for the case of degenerate optical parametric down conversion.

In the case of a 4.6 μm pump, phase matching was only predicted to occur for Type I ($e \rightarrow o o$) phase matching when limiting the wavelengths to those over which Eq. (2) is valid. In Fig. 14(b), the phase matching angle is seen to attain a maximum near 250K. Operation near the maximum is more temperature stable.

6. Summary

A temperature dependent Sellmeier equation for CdSiP₂ was obtained over a wide range of temperatures and wavelengths. A good match was obtained between the temperature dependent signal and idler wavelengths predicted by the equation and the experimentally measured values for two pump wavelengths. The dependence of the generated wavelengths on phase-matching angle and temperature was determined for various pump wavelengths.